

# Superconductivity suppression of $\text{Ba}_{0.5}\text{K}_{0.5}\text{Fe}_{2-2x}\text{M}_{2x}\text{As}_2$ single crystals by substitution of transition-metal ( $M = \text{Mn}, \text{Ru}, \text{Co}, \text{Ni}, \text{Cu}, \text{and Zn}$ )

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We investigated the doping effects of magnetic and nonmagnetic impurities on the single-crystalline  $p$ -type  $\text{Ba}_{0.5}\text{K}_{0.5}\text{Fe}_{2-2x}\text{M}_{2x}\text{As}_2$  ( $M = \text{Mn}, \text{Ru}, \text{Co}, \text{Ni}, \text{Cu}$  and  $\text{Zn}$ ) superconductors. The superconductivity indicates robustly against impurity of  $\text{Ru}$ , while weakly against the impurities of  $\text{Mn}, \text{Co}, \text{Ni}, \text{Cu}$ , and  $\text{Zn}$ . However, the present  $T_c$  suppression rate of both magnetic and nonmagnetic impurities remains much lower than what was expected for the  $s_{\pm}$ -wave model. The temperature dependence of resistivity data is observed an obvious low- $T$  upturn for the crystals doped with high-level impurity, which is due to the occurrence of localization. Thus, the relatively weak  $T_c$  suppression effect from  $\text{Mn}, \text{Co}, \text{Ni}, \text{Cu}$ , and  $\text{Zn}$  are considered as a result of localization rather than pair-breaking effect in  $s_{\pm}$ -wave model.

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## I. INTRODUCTION

The existence of Fe-based superconductor family arouses unexpected rapidly development<sup>1-3</sup>, for that is not only a second class of high- $T_c$  superconductors after the cuprate superconductors, but also because it is highly promising to understand the superconductivity (SC) mechanism of high- $T_c$  superconductors by comparing the two families. To data, it is probably the most crucial issue to confirm the pair-symmetry of the newly discovered superconductor, for which theoretical scientists proposed several possible models just after the discovery of the superconductors, among which the multi-gaped  $s$ -wave is generally acceptable, including the  $s_{\pm}$ <sup>4-6</sup> and  $s_{++}$  wave<sup>7-9</sup>. Both states represent the same hole Fermi pockets, while have opposite signs for the electron pockets, namely, the  $s_{\pm}$  wave is identified as a sign-reversal  $s$ -wave model, while a non-sign-reversal for the  $s_{++}$  state. Recently results from various experiments can hardly get a consensus for identifying which state is the real nature of this superconductor<sup>10-12</sup>. Meanwhile, the  $d$ -wave model with opposite signs for the nearest-neighbor electron pockets still remains competing with other models, once there are nodes on the hole pockets or even on both the electron and hole pockets<sup>6,13,14</sup>. More recently results suggested that different systems in the iron-pnictide family may represent different pair-symmetry types, even that the pair-symmetry can be quite different from material to material<sup>12</sup>. The varieties of the possible scenarios arouse further investigations, among which the impurity substitution is one of the most promising ways to ad-

dress the issue and even to uncover competing orders, because the pair-breaking mechanism from both magnetic and nonmagnetic impurities should be different for these models.

The iron-pnictide superconductor contains as common  $\text{Fe}_2\text{X}_2$  ( $X=\text{As}, \text{P}$  or  $\text{Se}$ ) planes, which is well-known as the superconducting layer. The substitution of point defect impurities for  $\text{Fe}$  is introduced for understanding the physical properties, like what was comprehensively studied in cuprates. According to Anderson's theorem, the nonmagnetic impurity (NMI) cannot break pairing in an isotropic SC gap but for an anisotropic gap<sup>15</sup>, while the pair-breaking effect of the magnetic impurities is independent of gap type. Thus, the nonmagnetic point defects are of great important. The  $\text{Zn}^{2+}$  with tightly closed  $d$ -shell is preferred as an ideal NMI<sup>16</sup>. Typically,  $\text{Zn}$  substitution for  $\text{Cu}$  was carried out over the last two decades on the cuprate superconductors such as  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ <sup>16-18</sup>,  $(\text{La},\text{Sr})_2\text{CuO}_4$ <sup>16,19-21</sup>, and  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ <sup>16,22-24</sup>. A few at.% of the  $\text{Zn}$  acts as a strong scattering center and remarkably depresses SC due to the  $d$ -wave anisotropic gap for cuprates<sup>16-24</sup>. Since the doped  $\text{Zn}$  often plays a crucial role of pairing symmetry determination of previous superconductors, we may expect that it works with the Fe-based superconductor as well.

Previous  $\text{Zn}$  studies for the Fe-based superconductor seem to be contradicted: Cheng *et al.* reported that the doped  $\text{Zn}$  can hardly affects SC of the  $p$ -type  $\text{Ba}_{0.5}\text{K}_{0.5}\text{Fe}_2\text{As}_2$ <sup>25</sup>, as Li *et al.* did in  $\text{LaFeAsO}_{0.85}\text{F}_{0.15}$ <sup>26</sup>. However, we found that the SC

was completely suppressed by at most 3 at.% of Zn for  $\text{LaFeAsO}_{0.85}$  once using high-pressure method<sup>27</sup>. Comparable result was obtained in the  $\text{K}_{0.8}\text{Fe}_{2-y-x}\text{Zn}_x\text{Se}_2$  superconductors<sup>28</sup>. Since the Zn substitution generally suffered from issue of the low melting point and high volatility<sup>23,24</sup>, it is uncertain that whether Zn has been successfully substituted into the Fe-site for previous polycrystals synthesized in ambient-pressure. Our recent studies indeed showed that more than 2 at.% of Zn were hardly doped into the *n*-type  $\text{Ba}(\text{Fe},\text{Co})_2\text{As}_2$  superconductor at ambient pressure condition<sup>29</sup>. In contrast, linear  $T_c$  suppression was found for the high-pressure prepared  $\text{BaFe}_{2-2x-2y}\text{Zn}_{2x}\text{Co}_{2y}\text{As}_2$  superconductors<sup>30</sup>. To avoid overestimation of the net Zn we proposed growing highly Zn-doped single crystals of the Fe-based superconductor by using a high-pressure technique.

In this study, we studied the impurities effect on the *p*-type  $(\text{Ba},\text{K})\text{Fe}_2\text{As}_2$  superconductors by a high-pressure and high-temperature method, for which magnetic and nonmagnetic elements around Fe were selected as the dopant, including 3*d* metals of Mn, Co, Ni, Cu and Zn, and Ru from 4*d*. The specific heat, magnetic and transport properties indicate that the SC is robustly against impurity of Ru, while weakly against the impurities of Mn, Co, Ni, Cu, and Zn.

## II. EXPERIMENTAL

Single-crystalline samples of  $\text{Ba}_{0.5}\text{K}_{0.5}\text{Fe}_2\text{As}_2$  (BK) and  $\text{Ba}_{0.5}\text{K}_{0.5}\text{Fe}_{2-2x}\text{M}_{2x}\text{As}_2$  ( $M = \text{Mn}$ ,  $x = 0.02$  and  $0.05$ ;  $M = \text{Ru}$ ,  $\text{Co}$ ,  $\text{Ni}$ ,  $\text{Cu}$  and  $\text{Zn}$ , nominal  $x = 0.05$ ,  $0.10$  and  $0.15$ ) were prepared in a high-pressure apparatus as reported elsewhere<sup>30</sup>. Here the start materials are BaAs (lab made), KAs (lab made), FeAs (lab made), Fe (3N), Mn (>99.9%), Ru (>99.9%), Co (>99.5%), Ni (>99.99%), Cu (>99.9%) and Zn (4N). Note that the pellet was self-separated into sizes of around  $0.3 \times 0.2 \times 0.1 \text{ mm}^3$  or much smaller after it left in vacuum for 2-3 days. The selected single crystals were held on a MgO substrate with *ab*-plane parallel with the substrate, and then cleaved into thin slices along *c*-axis as discussed in early report<sup>30</sup>. To confirm the impurity substitution the crystals were measured in an electron probe micro-analysis (EPMA, JXA-8500F, JEOL) soon after cleaved. Table 1 gives the real value of  $x$  for  $\text{Ba}_{0.5}\text{K}_{0.5}\text{Fe}_{2-2x}\text{M}_{2x}\text{As}_2$  ( $M = \text{Mn}$ ,  $\text{Ru}$ ,  $\text{Co}$ ,  $\text{Ni}$ ,  $\text{Cu}$  and  $\text{Zn}$ ) with start value of  $x = 0.05$ . The result demonstrates little difference from the starting materials, although a slightly less concentration for Mn, Ru, Ni and Zn. However, we will use the real concentration of  $x$  for the following analysis.

The cleaved single crystals were also studied by x-ray diffraction (XRD) method in the Rigaku Ultima-IV diffractometer using  $\text{CuK}\alpha$  radiation. The single crystals were also ground and studied by a powder XRD method, and the results indicated that the tetragonal  $\text{ThCr}_2\text{Si}_2$ -type structure ( $I4/mmm$ ) is formed over the compositions without second phase<sup>2,31</sup>.

In the DC magnetic susceptibility ( $\chi$ ) measurement, since the size of an individual crystal is too small to obtain accurate measurements, we loosely gathered small crystals ( $\sim 30 \text{ mg}$  in total) into a sample holder, and measured in Magnetic Properties Measurement System, Quantum Design. The sample was cooled down to 2 K without applying a magnetic field (zero-field-cooling, ZFC), followed by warming to 45 K in a field of 10 Oe and then cooled down again to 2 K (field-cooling, FC).

The cleaved single crystals were used for the in-plane DC electrical resistivity ( $\rho_{ab}$ ) measurement. To minimize the structure defects of the single crystals, we cleaved the crystals to  $\sim 1\text{-}10 \text{ }\mu\text{m}$  in thickness and cut them into a quadrature slices shape as  $\sim 100 \times 50 \text{ }\mu\text{m}^2$ . And then four terminals of the cleaved *ab*-plane were pasted with platinum wires by using silver paste. The  $\rho_{ab}$  was measured between 2 K and 300 K in Physical Properties Measurement System - 9 T, Quantum Design. Such cleaved single crystals were also measured the Hall coefficient ( $R_H$ ) in PPMS, where the electric current was along the *ab*-plane and  $H$  was applied parallel to *c*-axis. For the each sample with amount of 12-14 mg crystal, we measured the specific heat ( $C_p$ ) in PPMS-9T from 2 to 300 K by a heat-pulse relaxation method.

## III. RESULTS AND DISCUSSION

### A. X-ray diffraction

The XRD patterns for the cleavage plane of the separated crystals  $\text{Ba}_{0.5}\text{K}_{0.5}\text{Fe}_{1.9}\text{M}_{0.1}\text{As}_2$  ( $M = \text{Fe}$ ,  $\text{Mn}$ ,  $\text{Ru}$ ,  $\text{Co}$ ,  $\text{Ni}$ ,  $\text{Cu}$  and  $\text{Zn}$ , which are abbreviated as BK, BK-Mn, BK-Ru, BK-Co, BK-Ni, BK-Cu and BK-Zn, respectively) are shown in Fig. 1(a). The obvious orientation toward  $[0 \ 0 \ 2n]$  ( $n$  is integer) indicates that the cleavage plane is the *ab*-plane of the  $\text{ThCr}_2\text{Si}_2$ -type structure. Note that the main peak (0 0 8) for every impurity-doped crystals indicates an obvious shift in  $2\theta$  as shown in Fig. 1(b), suggesting that the impurities were indeed doped into the crystal lattice. The lattice parameters obtained by assuming the same structure for the powder XRD data are summarized in Table 1, as can be seen that the impurity-doping results in change for lattice parameters of both  $a$  and  $c$ . The unsystematic change in peak shift and lattice parameters seem unlike due to the basic change in size of doping ions. However, the difference between Fe-As and  $M$ -As bond size was considered as a crucial factor as discussed in Ref. 15. In addition, a magnetic effect is possibly included in the *c*-axis expansion<sup>32</sup>, especially for the nonmagnetic Zn ions, which results in nearly isotropic expansion for both  $a$  and  $c$ . Comparably, Zn-doped  $\text{BaFe}_{1.91-x}\text{Zn}_x\text{Co}_{0.11}\text{As}_2$ <sup>30</sup> and  $\text{YBa}_2\text{Cu}_{3-3x}\text{Zn}_{3x}\text{O}_{7-\delta}$ <sup>33</sup> also results in an isotropic expansion of the lattice.

TABLE I. The columns give the parameters (from left to right) of  $\text{Ba}_{0.5}\text{K}_{0.5}\text{Fe}_{2-2x}\text{M}_{2x}\text{As}_2$  ( $M = \text{Fe, Mn, Ru, Co, Ni, Cu}$  and  $\text{Zn}$ , nominal  $x=0.05$ ): real atomic concentration of  $M(x)$  from the EPMA measurement, lattice parameters of  $a$  and  $c$  from powder XRD,  $T_{c\rho}$  from resistivity data, and  $\Delta C_p/T_{c\rho}$ . The samples of  $\text{Ba}_{0.5}\text{K}_{0.5}\text{Fe}_{2-2x}\text{M}_{2x}\text{As}_2$  ( $M = \text{Fe, Mn, Ru, Co, Ni, Cu}$  and  $\text{Zn}$ ) are abbreviated to BK, BK-Mn, BK-Ru, BK-Co, BK-Ni, BK-Cu and BK-Zn, respectively.

Samples	$M(x)$	$a$ (Å)	$c$ (Å)	$T_{c\rho}$ (K)	$\Delta C_p/T_{c\rho}$ (mJ mol <sup>-1</sup> K <sup>-2</sup> )
BK	/	4.014(2)	13.298(2)	37.78	44.50
BK-Mn	0.039(2)	3.984(1)	13.196(3)	9.53	/
BK-Ru	0.032(6)	4.051(1)	13.419(4)	37.14	73.49
BK-Co	0.052(2)	4.038(1)	13.383(4)	30.31	39.26
BK-Ni	0.039(4)	3.990(1)	13.229(1)	26.75	/
BK-Cu	0.044(1)	3.970(1)	13.050(5)	22.29	/
BK-Zn	0.040(2)	4.102(2)	13.322(3)	30.15	21.66

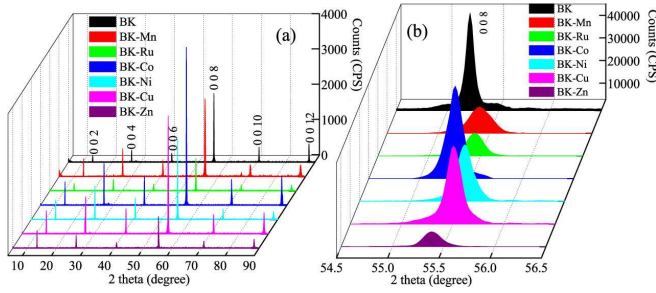


FIG. 1. XRD pattern of the single crystals  $\text{Ba}_{0.5}\text{K}_{0.5}\text{Fe}_{2-2x}\text{M}_{2x}\text{As}_2$  ( $M = \text{Mn, Ru, Co, Ni, Cu}$  and  $\text{Zn}$ , real  $x$  values are shown in Table 1).

## B. Magnetic measurement

Fig. 2 shows  $T$  dependence of the  $\text{Ba}_{0.5}\text{K}_{0.5}\text{Fe}_2\text{As}_2$  and  $\text{Ba}_{0.5}\text{K}_{0.5}\text{Fe}_{2-2x}\text{M}_{2x}\text{As}_2$  ( $M = \text{Mn, Ru, Co, Ni, Cu}$  and  $\text{Zn}$ ), where the impurity concentration of  $x$  is obtained from the EPMA measurements. The host crystal BK shows the maximum  $T_c$  of 38 K as reported elsewhere<sup>2</sup>. Obviously, the SC of  $\text{Ba}_{0.5}\text{K}_{0.5}\text{Fe}_2\text{As}_2$  shows strong against with the Ru impurity, which is accordance with the previous studies on the Ru substitution effect on  $\text{LaFeAsO}_{1-x}\text{F}_x$ <sup>34</sup> and  $\text{NdFeAsO}_{0.89}\text{F}_{0.11}$  superconductors<sup>35</sup>. The magnetic impurity of Mn indicates the sharpest  $T_c$  suppression among all impurities. It is surprising that the  $T_c$ -reduction effect from the 3d transition metals (Co, Ni, Cu and Zn) are similar each other, regardless of magnetic or nonmagnetic impurities.

## C. Transport property

Transport properties provide direct information for the influence of impurities or defects on various SC properties, including the carrier properties, coupling between charges, spin degrees of freedom, and more importantly the pair-breaking symmetry<sup>16,17</sup>. To obtain a reliable transport data high-quality single crystals are essential

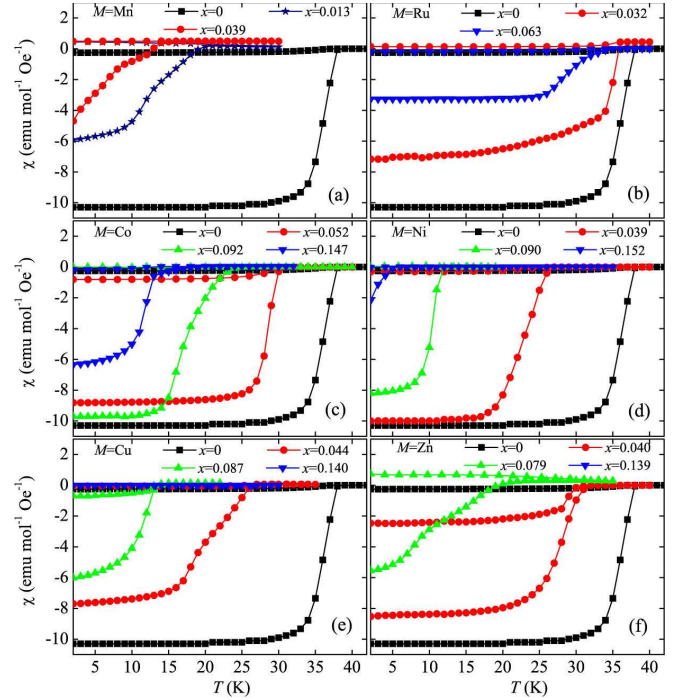


FIG. 2.  $\chi$  vs.  $T$  for  $\text{Ba}_{0.5}\text{K}_{0.5}\text{Fe}_{2-2x}\text{M}_{2x}\text{As}_2$  ( $M = \text{Mn, Ru, Co, Ni, Cu}$  and  $\text{Zn}$ ) at  $H = 10$  Oe.

with substitution of impurities. Fig. 3 shows the temperature dependence of  $ab$ -plane resistivity ( $\rho$ ) for the  $\text{Ba}_{0.5}\text{K}_{0.5}\text{Fe}_{2-2x}\text{M}_{2x}\text{As}_2$  ( $M = \text{Fe, Mn, Ru, Co, Ni, Cu}$  and  $\text{Zn}$ ). The  $T_c$  was defined from the peak value for the plots of  $d\rho/dT$  vs.  $T$ . It is clearly observed that  $T_c$  goes down with substitution of Mn, Co, Ni, Cu and Zn, while is weakly suppressed by Ru, well accordance with the magnetic results. Note that for the  $\text{Ba}_{0.5}\text{K}_{0.5}\text{Fe}_{2-2x}\text{Mn}_{2x}\text{As}_2$  ( $x = 0, 0.013$  and  $0.039$ ), the  $\rho$ - $T$  curves are almost parallel each other at the high- $T$  region as above  $T_c$ . Such behavior establishes that the hole content is modified by the defects rather than the electron irradiation. At low- $T$  on the other hand, an upturn in the  $\rho$ - $T$  curve is observed with substitution of defect content ( $x < 0.05$ ). This phenomenon has been often interpreted



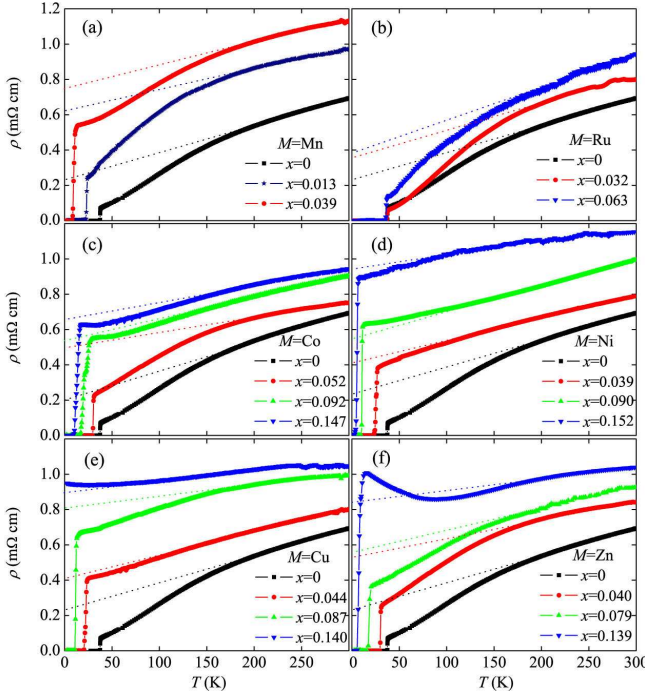


FIG. 3.  $\rho$  vs.  $T$  for  $\text{Ba}_{0.5}\text{K}_{0.5}\text{Fe}_{2-2x}\text{M}_{2x}\text{As}_2$  ( $M = \text{Mn, Ru, Co, Ni, Cu}$  and  $\text{Zn}$ ).

as the occurrence of localization. In case of Ru-doped crystals, the  $\rho$ - $T$  curves show almost parallel upturn with substitution of Ru at both high- and low- $T$  regions, suggesting the absence of localization. The  $\rho$ - $T$  curves for the Co, Ni, Cu and Zn-doped crystals are observed no parallel shift from that of the impurity-free crystal. However, the low- $T$  upturns of the resistivity appear for the impurity-doped crystals due to localization, regardless of magnetic or nonmagnetic impurities. Typically, the high-level Zn-doped crystals  $\text{Ba}_{0.5}\text{K}_{0.5}\text{Fe}_{2-2x}\text{Zn}_{2x}\text{As}_2$  ( $x = 0.139$ ) indicates a dramatically low- $T$  upturn from localization, similar phenomenon was observed in the Zn-substituted  $A(\text{Fe,Zn,Co})_2\text{As}_2$  superconductors<sup>30,36</sup>.

As the resistance of the superconductor shows a metal-like behavior, it decreases linearly with temperature at high-temperature regions. Therefore, we define the residual resistivity  $\rho_0$  by the extrapolation of  $T$ -linear resistivity to 0 K for the linear  $T$ -dependence at high- $T$  region. The residual resistivity  $\rho_0$  gradually increased with increasing doping level except Ru, and the increasing rate of  $\rho_0$  with  $x$  are  $\sim 98.2, 22.3, 42.8, 46.2$  and  $35.1 \mu\Omega\text{cm}/\%$  for Mn, Co, Ni, Cu and Zn, respectively. The residual resistivity is due to defect scattering, although it is not easy to obtain accurate determinations of the scattering rate directly from resistivity data, an alternative approach is to seek information from the decrease of  $T_c$  induced by the scattering centers<sup>16</sup>. Fig. 4 shows the residual resistivity  $\rho_0$  dependence of  $\Delta T_c$ , where the  $T_c$  data are from resistivity measurements. The  $T_c$  is gradually suppressed with increasing  $\rho_0$  for all impurities except Ru. The  $T_c$  is nearly independent of  $\rho_0$  for the substitution

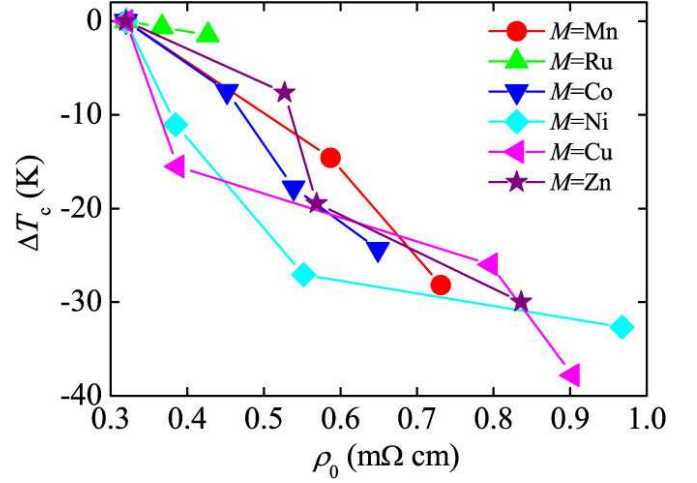


FIG. 4.  $\Delta T_c$  as a function of residual resistivity ( $\rho_0$ ) for the superconductors of  $\text{Ba}_{0.5}\text{K}_{0.5}\text{Fe}_{2-2x}\text{M}_{2x}\text{As}_2$  ( $M = \text{Mn, Ru, Co, Ni, Cu}$  and  $\text{Zn}$ ).

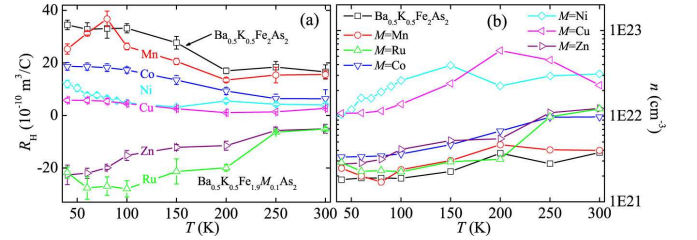


FIG. 5. (a) Hall coefficient ( $R_H$ ) vs.  $T$  and (b) carrier density ( $n$ ) vs.  $T$  for single-crystalline  $\text{Ba}_{0.5}\text{K}_{0.5}\text{Fe}_{2-2x}\text{M}_{2x}\text{As}_2$  ( $M = \text{Fe, Mn, Ru, Co, Ni, Cu}$  and  $\text{Zn}$ , real  $x$  values are shown in Table 1).

of Ru, while suppressed by impurities of Mn, Co, Ni, Cu and Zn as suppression rate of 66.77, 76.78, 46.43, 51.67 and 59.45 K/ $\mu\Omega\text{cm}$ , respectively. Note that these impurities are observed as similar suppression rate. However, the theoretical residual resistivity per 1% impurity with delta-functional strong potential is just  $\sim 20 \mu\Omega\text{cm}$ , and SC will also vanish with doping 1% of either magnetic or nonmagnetic impurities for the  $s_{\pm}$  wave model<sup>7-9</sup>. Consequently, the suppression rate is around 1900 K/ $\mu\Omega\text{cm}$ , indicating that the impurity scattering cross section is enlarged by the many-body effect, other than the pair-breaking effect<sup>37</sup>, which we will discuss in detail in the discussion part.

Fig. 5 shows the  $T$  dependence of Hall coefficient ( $R_H$ ) and carrier density ( $n$ ) for the BK, BK-Mn, BK-Ru, BK-Co, BK-Ni, BK-Cu and BK-Zn single crystals. The data for the impurity-free crystal accesses to the early data [25,37]. With substitution of 5 at.% of Mn, Co, Ni or Cu, the BK crystal is observed slightly reducing in  $R_H$ , while increasing carrier density. Sato and co-workers<sup>10,34,35</sup> proposed that the decrease in the absolute magnitude of  $R_H$  is due to the weakening of the magnetic fluctuations, as in the case of the thermoelectric power  $S$ . However,

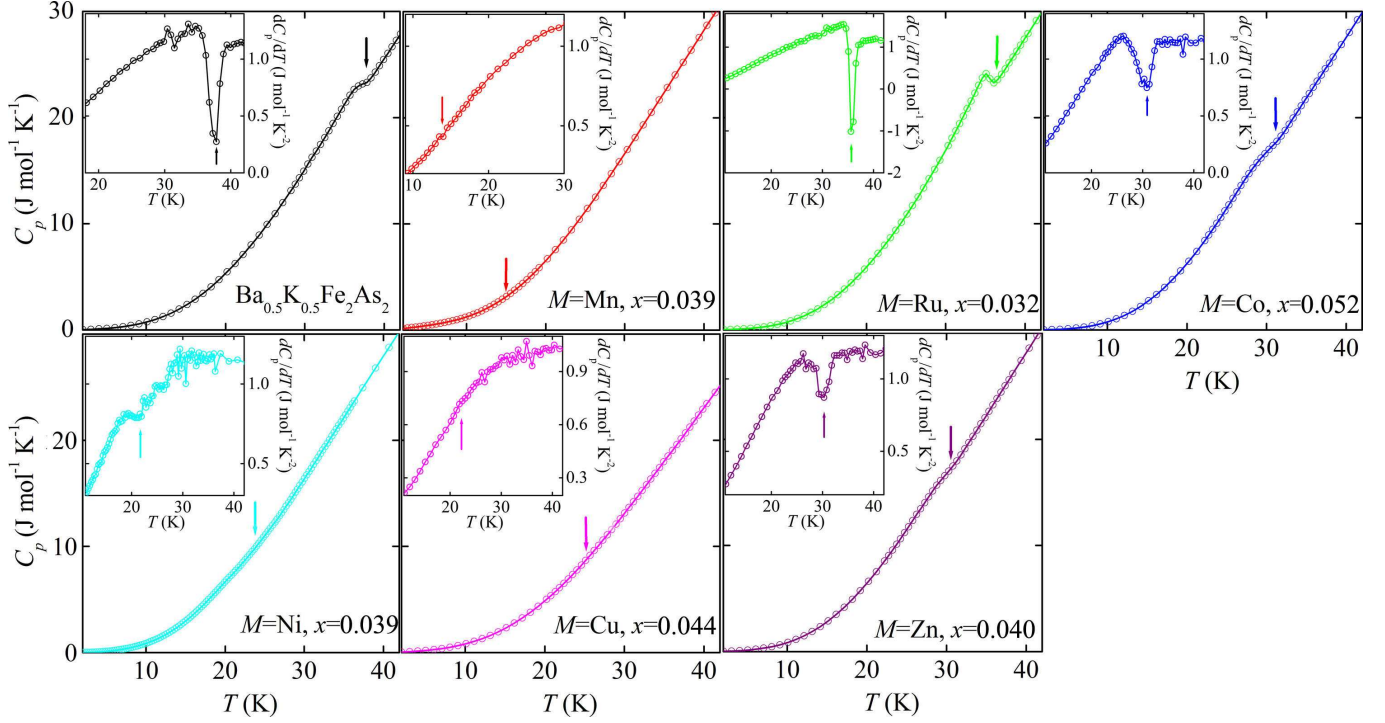


FIG. 6. Specific heat dependence of the temperature for  $\text{Ba}_{0.5}\text{K}_{0.5}\text{Fe}_{2-2x}\text{M}_{2x}\text{As}_2$  ( $M = \text{Mn, Ru, Co, Ni, Cu}$  and  $\text{Zn}$ ), where inset of each figure demonstrates the derivation of  $C_p$  to  $T$ , and the arrows indicate the heat capacity anomaly.

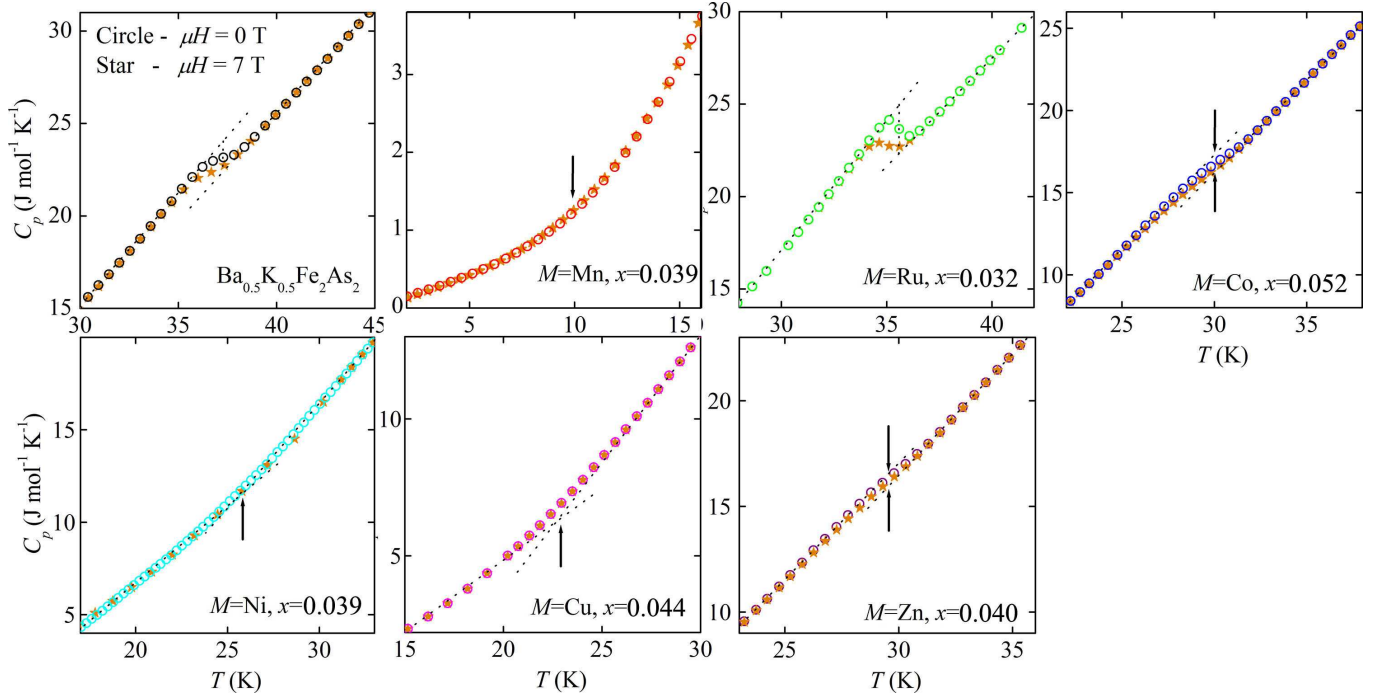


FIG. 7. Specific heat dependence of the temperature for  $\text{Ba}_{0.5}\text{K}_{0.5}\text{Fe}_{2-2x}\text{M}_{2x}\text{As}_2$  ( $M = \text{Mn, Ru, Co, Ni, Cu}$  and  $\text{Zn}$ ) with and without magnetic field of 7 T.

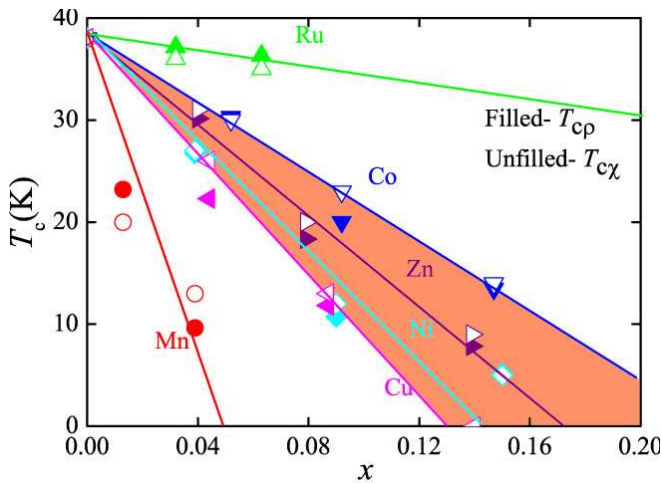


FIG. 8.  $T_c$  vs.  $x$  for the superconductors of  $\text{Ba}_{0.5}\text{K}_{0.5}\text{Fe}_{2-2x}\text{M}_{2x}\text{As}_2$  ( $M = \text{Mn, Ru, Co, Ni, Cu}$  and  $\text{Zn}$ ).

it is surprisingly that the impurities of Ru and Zn result in a negative  $R_H$ , which seems like that the introduction of Ru and Zn ions yield the charge carrier type from hole-doping to electron-doping. For the normal state, we found there is no significant change over various substitutes, indicating that the transition-metal substitution do not substantially alter the actual carrier density. This is reasonable because the substitution is isovalent. Regarding the previous impurity effect on charge carrier of both Fe-based and Cu-based superconductors, fairly little change was observed in the  $R_H$  measurements as well<sup>30,33</sup>. The actual carrier density change by transition-metal impurities does not account for the systematic  $T_c$  decrease<sup>5</sup>.

#### D. Specific heat data

The temperature dependent specific heat ( $C_p$ ) in zero-field for the BK, BK-Mn, BK-Ru, BK-Co, BK-Ni, BK-Cu and BK-Zn are given in Fig. 6, where inset of each figure demonstrates the derivation of  $C_p$  to  $T$ . Obvious heat capacity anomaly, indicated by the arrow, is associated well with the SC transition temperature for BK, BK-Ru, BK-Co, BK-Ni, and BK-Zn. However, there is almost absence of anomaly at  $T_c$  for the BK-Mn and BK-Cu. It is possible that disorder regarding impurity distribution causes inhomogeneous SC states, much broadening the expected peak, and the broad anomaly is masked by the lattice contributions<sup>39,40</sup>. In addition, it was found that the character of the anomaly is strongly doping dependence<sup>41</sup>. However, the reason for the absence of anomaly in Mn-, Ni-, and Cu-substituted samples need further investigation. Fig. 7 shows the  $C_p$ - $T$  curves in both fields of 0 and 7 T at around  $T_c$ , from which we estimate the specific heat jump ( $\Delta C_p/T_{cp}$ ) for these transitions at zero-field as shown in Table 1, where

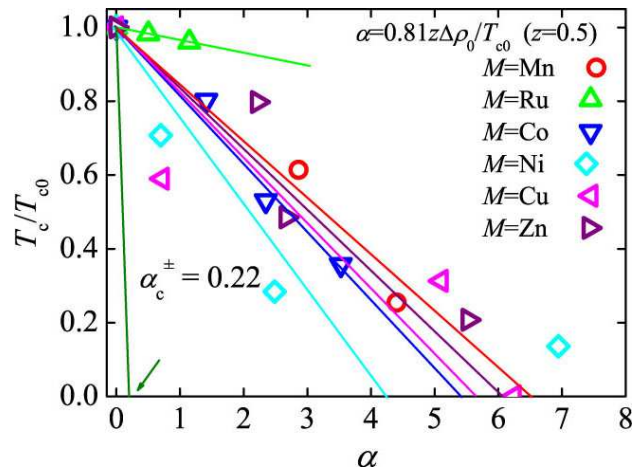


FIG. 9.  $T_c/T_{c0}$  vs.  $\alpha$  with various calculations for  $\text{Ba}_{0.5}\text{K}_{0.5}\text{Fe}_{2-2x}\text{M}_{2x}\text{As}_2$  ( $M = \text{Mn, Co, Ni, Cu}$  and  $\text{Zn}$ ). The  $T_c$  of each impurity-doped sample is normalized with  $T_{c0}$  of the impurity-free compound. The pair-breaking rate  $\alpha$  is estimated as  $\alpha = 0.88z\Delta\rho_0/T_{c0}$ , where  $\Delta\rho_0$  is the difference of the residual resistivity from that of impurity-free crystals, and  $z$  is the renormalization factor, for which we take  $z = 0.5$  from ARPES in 122 superconductor<sup>43,44</sup>.

$T_{cp}$  is the  $T_c$  estimated from resistivity data. It is observed that the impurities substitution change weakly on superconducting phase as judged from the size of specific heat jump, although the Co and Zn substitution reduced weakly on  $\Delta C_p/T_{cp}$ , as well as the Ru-doping enhances the  $\Delta C_p/T_{cp}$  (73.49 mJ mol<sup>-1</sup> K<sup>-2</sup>) to about two times of the impurity-free sample (44.50 mJ mol<sup>-1</sup> K<sup>-2</sup>). On the other hand, the applied magnetic field of 7 T is not large enough to suppress the anomaly (see Fig. 7) due to the high upper critical fields ( $> 55$  T). Since both the superconducting temperature and the upper critical fields in these superconductors are relatively high, we can hardly make a reliable estimate of the normal state electronic specific heat.

#### IV. DISCUSSION

We have described the influence of impurities on the magnetic, transport and specific heat properties in the  $\text{Ba}_{0.5}\text{K}_{0.5}\text{Fe}_2\text{As}_2$  superconductor. On basis of these results, we focus on the discussion of pair-breaking effects in terms of both  $s_{\pm}$  and  $s_{++}$  wave states.

Based on density functional calculations it was found that the impurity effects in iron-based superconductors can be classified into three groups according to the derived parameters: (i) Mn (0.3 eV), Co (-0.3 eV), and Ni (-0.8 eV), (ii) Ru (0.1 eV) and (iii) Zn (-8 eV)<sup>42</sup>. Among these impurities the nonmagnetic Zn works as a unitary scattering potential that is comparable to the bandwidth, as a result of the quite strong potential. Consequently, it is expected as strictly pair-breaking effect on the anisotropic SC gaps. According to Ref. 7 the reduc-



tion in  $T_c$  due to strong impurity potential in the  $s_{\pm}$  wave state is  $\sim 50z$  K/%, where  $z$  is the renormalization factor ( $= m/m^*$ ;  $m$  and  $m^*$  are the band-mass and the effective mass, respectively). The effective mass was estimated as  $2m_e$  from ARPES in 122 superconductor<sup>43,44</sup>, thus we obtain the suppression rate of 25 K/% for  $z = 0.5$ . In contrast, the  $T_c$  would be weakly suppressed by impurities in the  $s_{++}$  wave state, due to the following reasons: (i) suppression of the orbital fluctuations, which is a possible origin of the  $s_{++}$  wave state, because of the violation of the orbital degeneracy near the impurities, and (ii) the strong localization effect in which the mean-free-path is comparable to the lattice spacing<sup>7</sup>. These may account for the observed  $T_c$  decrease. In our present results, the decrease of the  $\chi$  and  $\rho$ -defined  $T_c$  ( $T_{c\chi}$  and  $T_{c\rho}$ ) with doping level  $x$  for the superconductors of  $\text{Ba}_{0.5}\text{K}_{0.5}\text{Fe}_{2-2x}\text{M}_{2x}\text{As}_2$  ( $M = \text{Mn, Ru, Co, Ni, Cu}$  and  $\text{Zn}$ ) is given in Fig. 8. We estimated the suppression rate of Zn is 2.22 K/% by applying a linear function to the  $T_{c\rho}$  vs.  $x$ , which is well accordance with the  $\text{BaFe}_{1.89-2x}\text{Zn}_{2x}\text{Co}_{0.11}\text{As}_2$  superconductors<sup>30</sup>. The observed robustness of SC seems like to contradict with the nonmagnetic impurity quantitatively in the  $s_{\pm}$  wave model. Applied a linear function to the  $T_{c\rho}$ - $x$ , the suppression rates for Mn, Ru, Co, Ni, and Cu are 6.98, 0.27, 1.73, 2.21 and 2.68 K/%, respectively. Among these impurities Mn is observed as the strongest suppression effects, even though such influence is quite weaker than what was expected from the  $s_{\pm}$  wave model. The negligible suppression effect from Ru in present compound is consistent with in the 1111-system<sup>10,45</sup>. The other transition metal impurities show less difference in suppression effect with Zn.

On basis of previous pair-breaking analysis in the  $\text{BaFe}_{1.89-2x}\text{Zn}_{2x}\text{Co}_{0.11}\text{As}_2$  superconductors<sup>30</sup>, we calculated the pair-breaking rate  $\alpha = z\hbar\gamma/2\pi k_B T_{c0}$  for  $\text{Ba}_{0.5}\text{K}_{0.5}\text{Fe}_{2-2x}\text{M}_{2x}\text{As}_2$  ( $M = \text{Mn, Ru, Co, Ni, Cu}$  and  $\text{Zn}$ ), where  $T_{c0}$  is the  $T_c$  of the impurity-free compound, and  $\gamma$  is the electron scattering rate. Previous theoretical study proposed a relation between  $\gamma$  and  $\Delta\rho_0$  as  $\Delta\rho_0$  ( $\mu\Omega\text{cm}$ ) =  $0.18\gamma$  (K) in terms of five-orbital model for 122 systems, here  $\Delta\rho_0$  is the difference of the residual resistivity of the impurity-doped and impurity-free crystals. For the  $s_{\pm}$ -wave state, the SC should vanish in the range  $\alpha > \alpha_c^{\pm} = 0.22^7$ . For the present experiment, we estimated  $\alpha = 0.88z\Delta\rho_0/T_{c0}$  by using  $z = 0.50$  as shown in Fig. 9. The  $T_c/T_{c0}$  vs.  $\alpha$  data change in roughly linear; thereby we applied a linear function to the data and estimated the critical pair-breaking parameters as 6.52, 5.23, 4.24, 5.41 and 6.05 for impurities of Mn, Co, Ni, Cu and Zn, re-

spectively. Comparably result was obtained for the pair-breaking effect of Zn in the  $\text{BaFe}_{1.89-2x}\text{Zn}_{2x}\text{Co}_{0.11}\text{As}_2$  superconductors as  $\alpha = 11.49$  with  $z = 0.5$ . Resent data for the proton irradiated  $\text{Ba}(\text{Fe,Co})_2\text{As}_2$  showing similar results as those of our chemical doping<sup>46</sup>. Obviously, the pair-breaking parameters experimentally estimated for the present compound are far above the limit  $\alpha_c^{\pm} = 0.22$  for the  $s_{\pm}$ -wave model, suggesting that the realization of the  $s_{++}$  wave state rather than the  $s_{\pm}$ -wave model in the 122-type Fe-based superconductor.

## V. CONCLUSIONS

To summarize, we have studied the superconductivity suppression effect on  $\text{Ba}_{0.5}\text{K}_{0.5}\text{Fe}_{2-2x}\text{M}_{2x}\text{As}_2$  single crystals by substitution of transition-metal ( $M = \text{Mn, Ru, Co, Ni, Cu}$ , and  $\text{Zn}$ ). The superconductivity of the  $p$ -type iron-based superconductor shows robustly against impurity of Ru, while weakly against the impurities of Mn, Co, Ni, Cu, and Zn, whose  $T_c$  suppression rate are 6.98, 1.73, 2.21, 2.68, and 2.22 K/%, respectively. Mn is observed as the strongest suppression effects, while the other transition metal impurities of Co, Ni, Cu, and Zn show similar suppression effect regardless of magnetic or nonmagnetic property. However, the present  $T_c$  suppression rate of both magnetic and nonmagnetic impurities remains much lower than what is expected for the  $s_{\pm}$ -wave model. The temperature dependence of resistivity data was observed an obviously low- $T$  upturn for the high-level impurity-doped crystals, which is due to the occurrence of localization. The relatively weak  $T_c$  suppression effect from Mn, Co, Ni, Cu, and Zn are considered as a result of localization rather than pair-breaking effect in  $s_{\pm}$ -wave model. However, another scenario toward the non-sign reversal  $s$ -wave model ( $s_{++}$ -wave) is more likely for the present superconductors.

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<sup>1</sup> Y. Kamihara, T. Watanabe, M. Hirano, and H. Hosono, J. Am. Chem. Soc. **130**, 3296 (2008).

<sup>2</sup> M. Rotter, M. Tegel, and D. Johrendt, Phys. Rev. Lett. **101**, 107006 (2008).

<sup>3</sup> Z. A. Ren, W. Lu, J. Yang, W. Yi, X. L. Shen, C. Zheng, G. C. Che, X. L. Dong, L. L. Sun, F. Zhou, and Z. X.

- Zhao, Chinese Phys. Lett. **25**, 2215 (2008).
- <sup>4</sup> I. I. Mazin, D. J. Singh, M. D. Johannes, and M. H. Du, Phys. Rev. Lett. **101**, 057003 (2008).
  - <sup>5</sup> I. I. Mazin, Nature **464**, 183(2010).
  - <sup>6</sup> K. Kuroki, S. Onari, R. Arita, H. Usui, Y. Tanaka, H. Kontani, and H. Aoki, Phys. Rev. Lett. **101**, 087004 (2008).
  - <sup>7</sup> S. Onari and H. Kontani, Phys. Rev. Lett. **103**, 177001 (2009).
  - <sup>8</sup> S. Onari, H. Kontani, and M. Sato, Phys. Rev. B **81**, 060504(R) (2010).
  - <sup>9</sup> T. Saito, S. Onari, and H. Kontani, Phys. Rev. B **82**, 144510 (2010).
  - <sup>10</sup> M. Sato, Y. Kobayashi, S. C. Lee, H. Takahashi, E. Satomi, and Y. Miura, J. Phys. Soc. Jpn. **79**, 014710 (2010).
  - <sup>11</sup> D. V. Efremov, M. M. Korshunov, O. V. Dolgov, A. A. Golubov, and P. J. Hirschfeld, Phys. Rev. B **84**, 180512(R) (2011).
  - <sup>12</sup> P. J. Hirschfeld, M. M. Korshunov, and I. I. Mazin, Rep. Prog. Phys. **74**, 124508 (2011).
  - <sup>13</sup> W. Q. Chen, K. -Y. Yang, Y. Zhou, and F. -C. Zhang, Phys. Rev. Lett. **102**, 047006 (2009).
  - <sup>14</sup> S. Maiti, M. M. Korshunov, T. A. Maier, P. J. Hirschfeld, and A.V. Chubukov, Phys. Rev. Lett. **107**, 147002 (2011).
  - <sup>15</sup> P. W. Anderson, J. Phys. Chem. Solids **11**, 26 (1959).
  - <sup>16</sup> H. Alloul, J. Bobroff, M. Gabay, and P. J. Hirschfeld, Rev. Mod. Phys. **81**, 45(2009).
  - <sup>17</sup> G. V. M. Williams, J. L. Tallon, and R. Dupree, Phys. Rev. B **61**, 4319 (2000).
  - <sup>18</sup> C. Bernhard, Ch Niedermayer, T. Blasius, G. V. M. Williams, R. De Renzi, C. Bucci, and J. L. Tallon, Phys. Rev. B **58**, 8937 (1998).
  - <sup>19</sup> M. -H. Julien, T. Fehér, M. Horvati, C. Berthier, O. N. Bakharev, P. Ségransan, G. Collin, and J. -F. Marucco, Phys. Rev. Lett. **84**, 3422 (2000).
  - <sup>20</sup> J. M. Tarascon, E. Wang, S. Kivelson, B. G. Bagley, G. W. Hull, R. Ramesh, Phys. Rev. B **42**, 218 (1990).
  - <sup>21</sup> N. P. Armitage, P. Fournier, and R. L. Greene, Rev. Mod. Phys. **82**, 2421 (2010).
  - <sup>22</sup> J. L. Tallon, Phys. Rev. B **58**, 5956 (1998).
  - <sup>23</sup> B. vom Hedt, W. Lisseck, K. Westerholt, and H. Bach, Phys. Rev. B **49**, 9898 (1994).
  - <sup>24</sup> Y. K. Kuo, C. W. Schneider, M. J. Skove, M. V. Nevitt, G. X. Tessema, and J. J. McGee, Phys. Rev. B **56**, 6201(1997).
  - <sup>25</sup> P. Cheng, B. Shen, J. P. Hu, and H. H. Wen, Phys. Rev. B **81**, 174529 (2010).
  - <sup>26</sup> Y. Li, J. Tong, Q. Tao, C. Feng, G. Cao, Z. Xu, W. Chen, and F. Zhang, New J. Phys. **12**, 083008 (2010).
  - <sup>27</sup> Y. F. Guo, Y. G. Shi, S. Yu, A. A. Belik, Y. Matsushita, M. Tanaka, Y. Katsuya, K. Kobayashi, I. Nowik, I. Felner, V. P. S. Awana, K. Yamaura, and E. Takayama-Muromachi, Phys. Rev. B **82**, 054506 (2010).
  - <sup>28</sup> D. Tan, C. Zhang, C. Xi, L. Ling, L. Zhang, W. Tong, Y. Yu, G. Feng, H. Yu, L. Pi, Z. Yang, S. Tan, and Y. Zhang, Phys. Rev. B **84**, 014502 (2011).
  - <sup>29</sup> J. J. Li, Y. F. Guo, S. B. Zhang, S. Yu, Y. Tsujimoto, K. Yamaura, and E. Takayama-Muromachi, Physica C **471**, 213(2011).
  - <sup>30</sup> J. Li, Y. Guo, S. Zhang, S. Yu, Y. Tsujimoto, H. Kontani, K. Yamaura, and E. Takayama-Muromachi, Phys. Rev. B **84**, 020513(R) (2011).
  - <sup>31</sup> F. Han, X. Zhu, P. Cheng, G. Mu, Y. Jia, L. Fang, Y. Wang, H. Luo, B. Zeng, B. Shen, L. Shan, C. Ren, and H.-H. Wen, Phys. Rev. B **80**, 024506 (2009).
  - <sup>32</sup> L. J. Zhang and D. J. Singh, Phys. Rev. B **80**, 214530 (2009).
  - <sup>33</sup> J. M. Tarascon, P. Barboux, P. F. Miceli, L. H. Greene, G. W. Hull, M. Eibschutz, and S. A. Sunshine, Phys. Rev. B **37**, 7458 (1988).
  - <sup>34</sup> E. Satomi, S. C. Lee, Y. Kobayashi, and M. Sato, J. Phys. Soc. Jpn., **79**, 094702 (2010).
  - <sup>35</sup> S. C. Lee, E. Satomi, Y. Kobayashi, and M. Sato, J. Phys. Soc. Jpn., **79**, 023702 (2010).
  - <sup>36</sup> J. Li, Y. Guo, S. Zhang, Y. Tsujimoto, X. Wang, C. I. Sathish, S. Yu, K. Yamaura, and E. Takayama-Muromachi, Solid State Commun. **152**, 671 (2012).
  - <sup>37</sup> H. Kontani and M. Ohno, Phys. Rev. B **74**, 014406 (2006).
  - <sup>38</sup> H. Q. Yuan, J. Singleton, F. F. Balakirev, S. A. Baily, G. F. Chen, J. L. Luo, and N. L. Wang, Nature **457**, 565 (2009).
  - <sup>39</sup> S. Nandi, M. G. Kim, A. Kreyssig, R. M. Fernandes, D. K. Pratt, A. Thaler, N. Ni, S. L. Bud'ko, P. C. Canfield, J. Schmalian, R. J. McQueeney, and A. I. Goldman, Phys. Rev. Lett. **104**, 057006 (2010).
  - <sup>40</sup> N. Ni, M. E. Tillman, J.-Q. Yan, A. Kracher, S. T. Hannahs, S. L. Bud'ko, and P. C. Canfield, Phys. Rev. B **78**, 214515 (2008).
  - <sup>41</sup> M. K. Yu and J. P. Franck, Phys. Rev. B **48**, 18 (1993).
  - <sup>42</sup> K. Nakamura, R. Arita, and H. Ikeda, Phys. Rev. B **83**, 144512 (2011).
  - <sup>43</sup> D. V. Evtushinsky, D. S. Inosov, V. B. Zabolotnyy, M. S. Viazovska, R. Khasanov, A. Amato, H. -H. Klauss, H. Luetkens, Ch. Niedermayer, G. L. Sun, V. Hinkov, C. T. Lin, A. Varykhalov, A. Koitzsch, M. Knupfer, B. Bchner, A. A. Kordyuk, and S. V. Borisenko, New J. Phys. **11**, 055069 (2009).
  - <sup>44</sup> K. Nakayama, T. Sato, P. Richard, Y. -M. Xu, Y. Sekiba, S. Souma, G. F. Chen, J. L. Luo, N. L. Wang, H. Ding, and T. Takahashi, Europhys. Lett. **85**, 67002 (2009).
  - <sup>45</sup> S. C. Lee, E. Satomi, Y. Kobayashi, and M. Sato, J. Phys. Soc. Jpn. **79**, 023702 (2010).
  - <sup>46</sup> Y. Nakajima, T. Taen, Y. Tsuchiya, T. Tamegai, H. Kitamura, and T. Murakami, Phys. Rev. B **82**, 220504(R) (2010).